REPORT DOCUMENTATION PAGE

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Recent Advances in Understanding the Reactivity of Energetic Ionic Liquids in Propulsion Applications

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14. ABSTRACT

The interest in using energetic ionic liquids (EILs) to replace highly toxic and volatile hydrazine-based fuels stems from the inherently low vapor pressure of ionic liquids. Understanding the reactivity of EILs in propulsion applications has included both experimental and theoretical investigations, but is complicated by the fast and complex chemistry involved during ignition and combustion of the propellants. Recently, the availability of a polarizable continuum model variant called the generic ionic liquid (GIL) model, developed by Truhlar and co-workers, has enabled the investigation of anion properties such as basicity and nucleophilicity in the condensed phase. Both the basicity and nucleophilicity of the anion influence the thermal decomposition of ionic liquids and understanding basicity of the anion is important in interpreting hypergolic ignition mechanisms in dicyanamide-based EILs. An approach using the GIL has been developed to understand both basicity and nucleophilicity trends in EILs, the results of which are presented in this paper. Also, recent experimental investigations using reactive surface scattering techniques and tunable vacuum ultraviolet photoionization of catalytically decomposed aerosols of EILs will be discussed.

15. SUBJECT TERMS

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Recent advances in understanding the reactivity of energetic ionic liquids in propulsion applications

Steven D. Chambreau

American Chemical Society Fall 2014 National Conference
August 12, 2014

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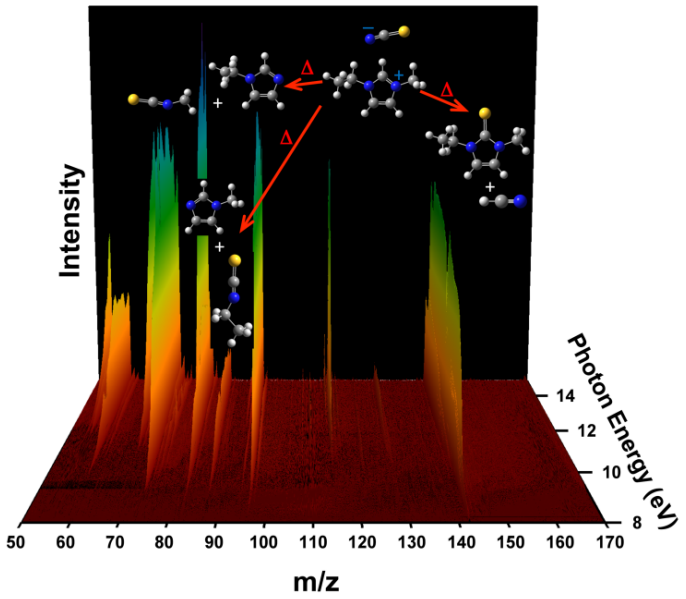

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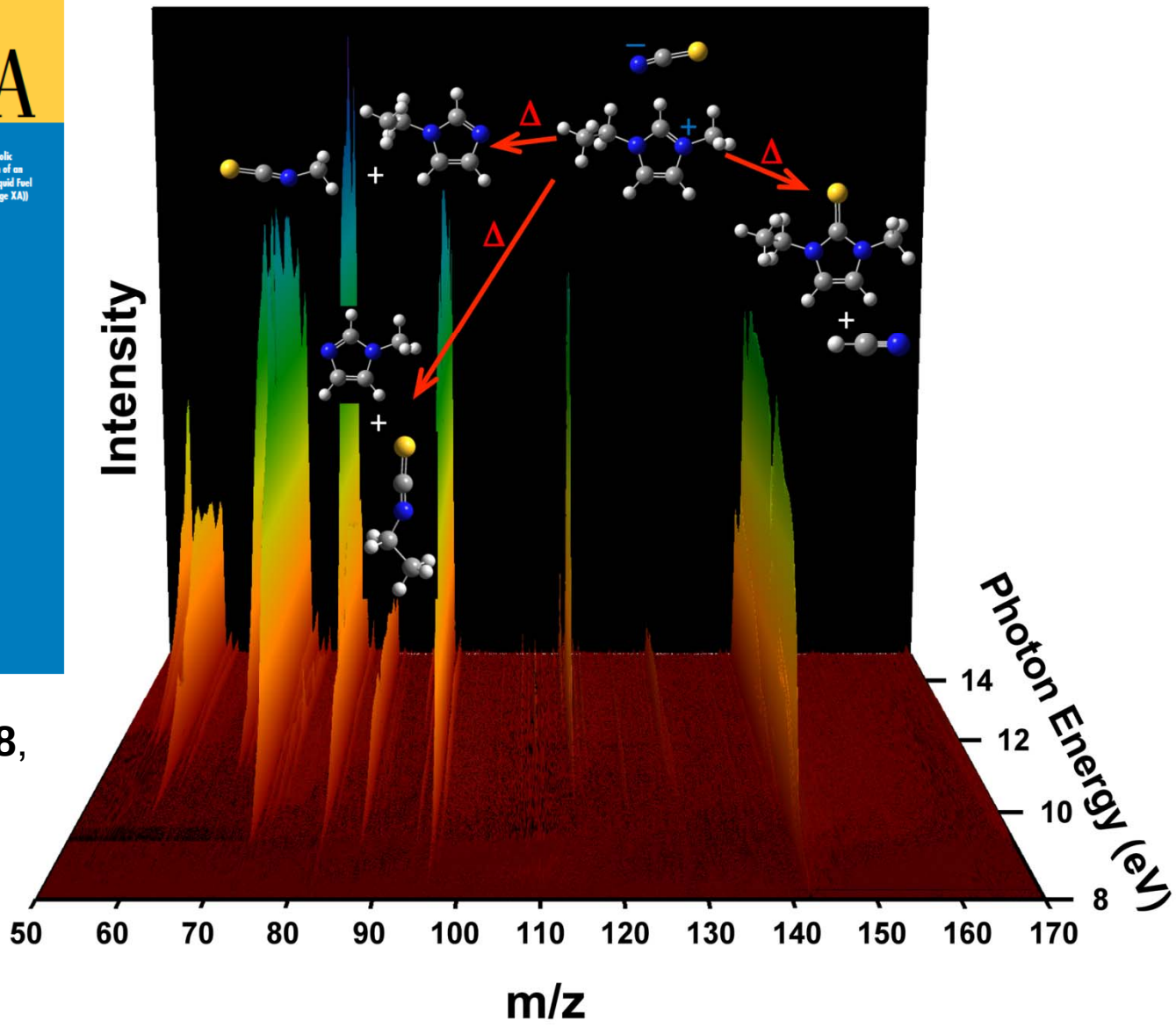
J. Phys. Chem. A, **2008**, *112*, 7816-7824.



J. Am. Chem. Soc., submitted **2014**

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Outline

- Introduction
- Thermal decomposition of ionic liquids
  - Basicity & nucleophilicity
    - gas phase vs. GIL model
- Reactive scattering
- VUV-PIMS of catalytic ionic liquid reactivity

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Motivation

- Replacement for monomethylhydrazine + N_2O_4

  (highly volatile and toxic!!)

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GIL model

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

Quantum Mechanical Continuum Solvation Models for Ionic Liquids

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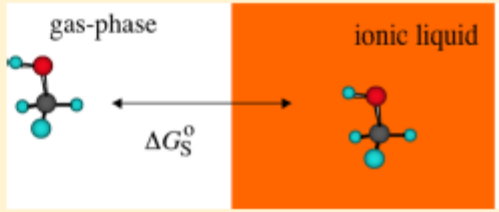
Supporting Information

ABSTRACT: The quantum mechanical SMD continuum universal solvation model can be applied to predict the free energy of solvation of any solute in any solvent following specification of various macroscopic solvent parameters. For three ionic liquids where these descriptors are readily available, the SMD solvation model exhibits a mean unsigned error of 0.48 kcal/mol for 93 solvation free energies of neutral solutes and a mean unsigned error of 1.10 kcal/mol for 148 water-to-IL transfer free energies. Because the necessary solvent parameters are *not* always available for a given ionic liquid, we determine average values for a set of ionic liquids over which measurements *have* been made in order to define a generic ionic liquid solvation model, SMD-GIL. Considering 11 different ionic liquids, the SMD-GIL solvation model exhibits a mean unsigned error of 0.43 kcal/mol for 344 solvation free energies of neutral solutes and a mean unsigned error of 0.61 kcal/mol for 431 water-to-IL transfer free energies. As these errors are similar in magnitude to those typically observed when applying continuum solvation models to ordinary liquids, we conclude that the SMD universal solvation model may be applied to ionic liquids as well as ordinary liquids.



J. Phys. Chem. B **2012**, 116, 9122−9129

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GIL model

- How do we predict basicity and nucleophilicity in any ionic liquid?
- GIL model is polarizable continuum model benchmarked to treat ionic liquids in general.

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Basicity: ΔG_{acid}

$HA \rightarrow H^+ + A^-$

	ΔG_{acid} (g)		ΔG_{acid} (l)		ΔG_{acid} (l)
	(kJ/mol)		SMD-GIL (kJ/mol)		SMD-H_2O (kJ/mol)
HNCS	1332.5	HNCS	607.0	HNCS	549.5
HNO_3	1306.7	HNCNCN	578.0	HNCNCN	521.8
HSCN	1274.2	HNO_3	566.6	NCNHCN	495.9
HNCNCN	1272.6	NCNHCN	550.3	HNO_3	494.9
NCNHCN	1234.6	HSCN	548.8	HSCN	492.6
HTCM (central)	1197.1	HTCM (central)	537.9	HTCM (central)	490.5
HTCM (terminal)	1188.7	HTCM (terminal)	533.9	HTCM (terminal)	483.9

basicity: $SCN^- > N(CN)_2^- > NO_3^- > TCM^-$

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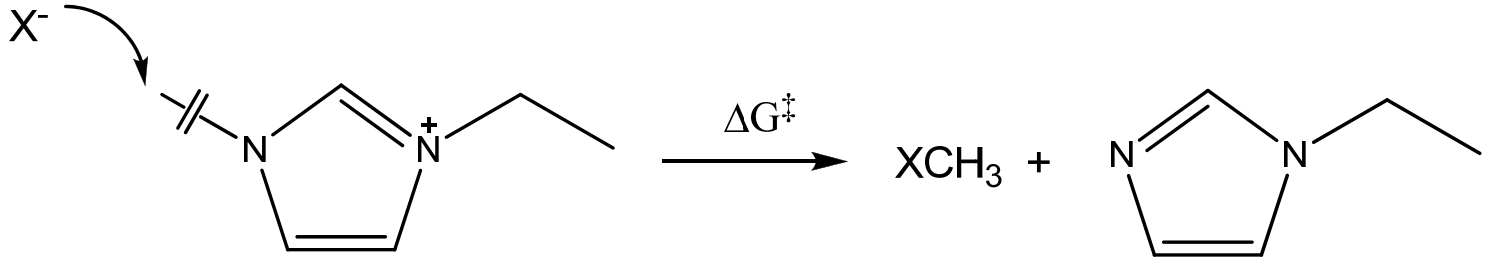
Anion Nucleophilicity

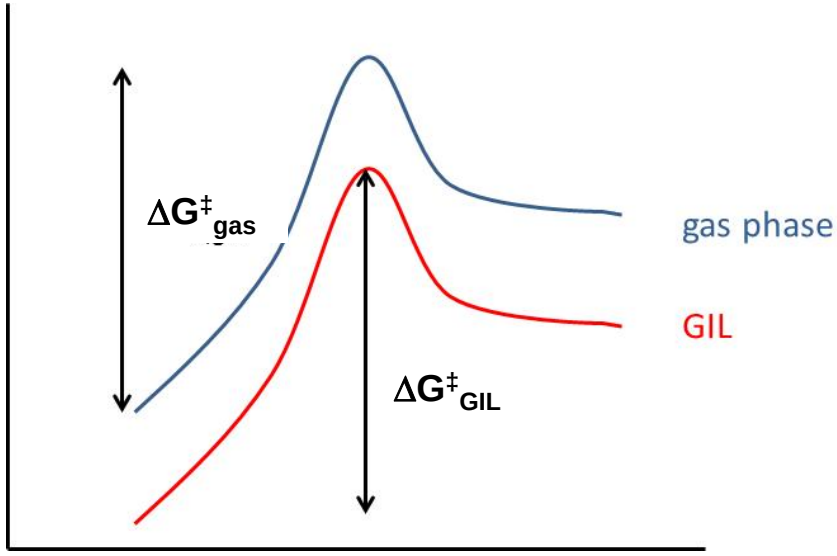


X = Br, SCN, dca, TCM

IL	method	$\Delta G^{\ddagger}$ (kJ/mol)	ΔG (gas-->liquid) (kJ/mol)
$EMIM^{+}Br^{-}$	M06	138.6	-6.5
	GIL	134.6	-4.0
$EMIM^{+}dca^{-}$	M06	163.6	-1.7
	GIL	158.2	-5.4
$EMIM^{+}SCN^{-}$	M06	151.2	-2.2
	GIL	153.4	2.2
$EMIM^{+}TCM^{-}$	M06	175.8	-0.8
	GIL	181.5	5.7

Nucleophilicity: $Br^{-} > SCN^{-} > dca^{-} > TCM^{-}$

The energy differences between the gas phase and GIL condensed phase species is approximately constant: ($E_{a,gas} \sim E_{a,GIL}$)



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Reactive scattering of HNO_3 off of $EMIM^+dca^-$

- Can we detect protonated dca^-?

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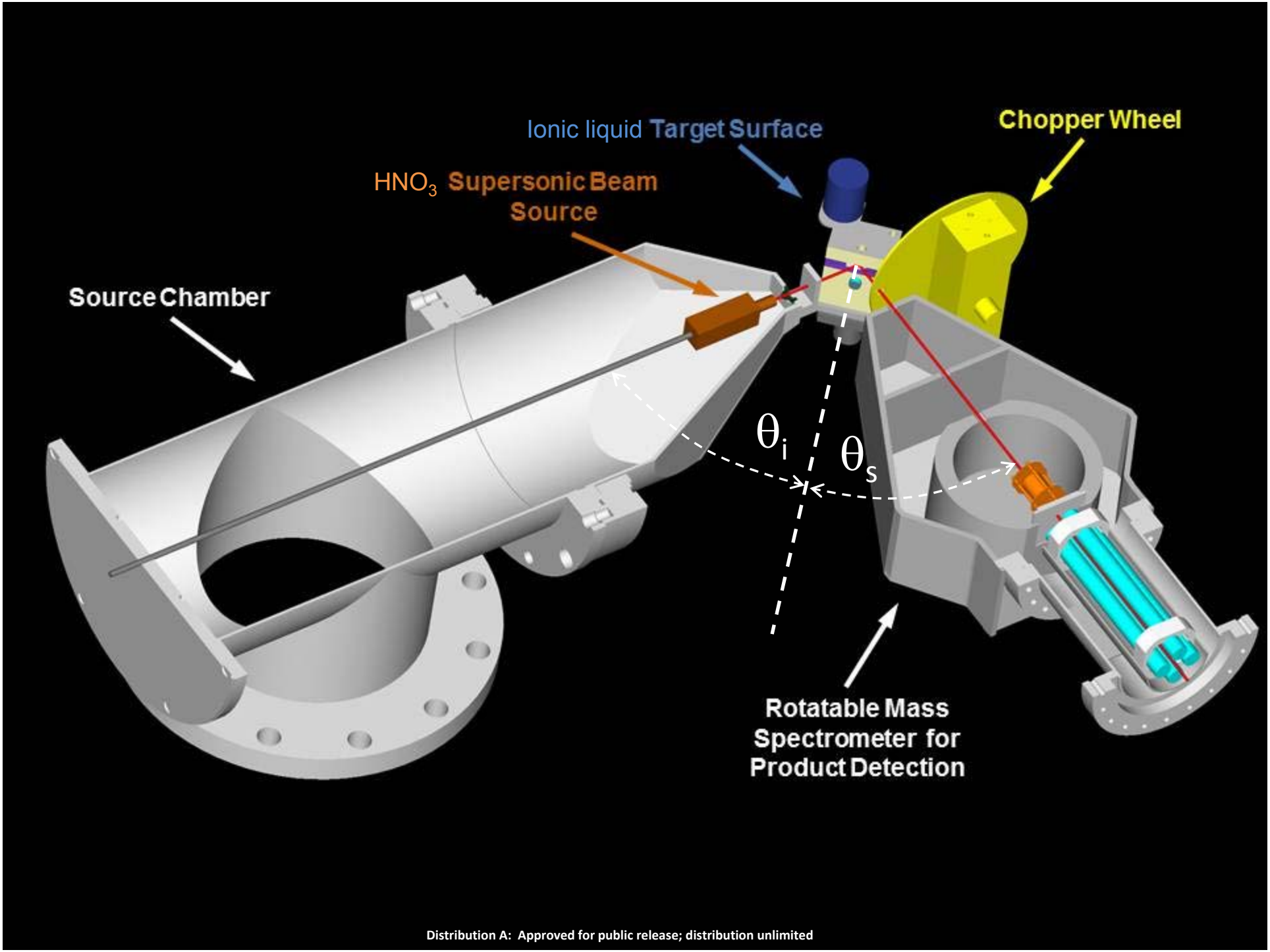

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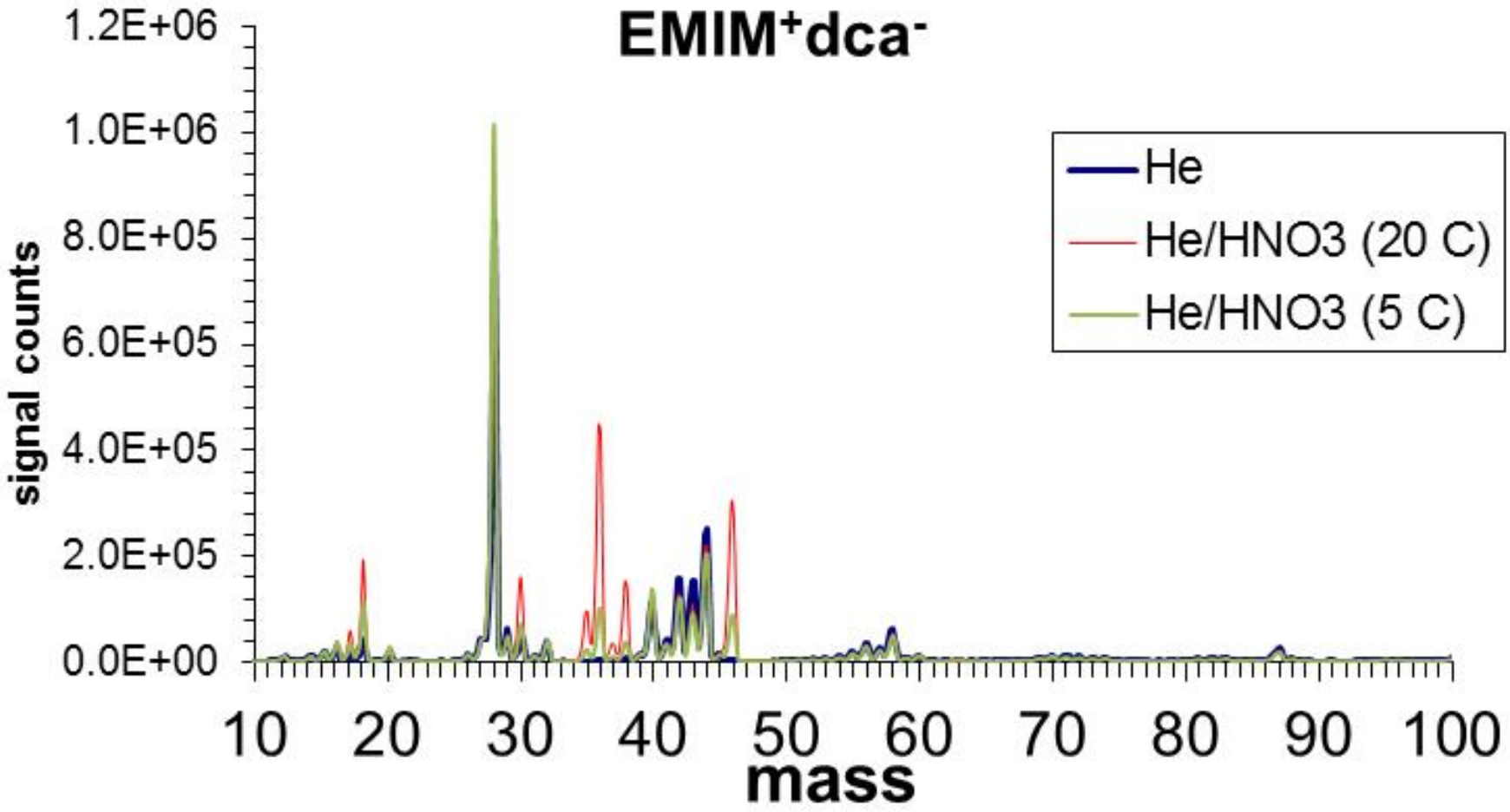

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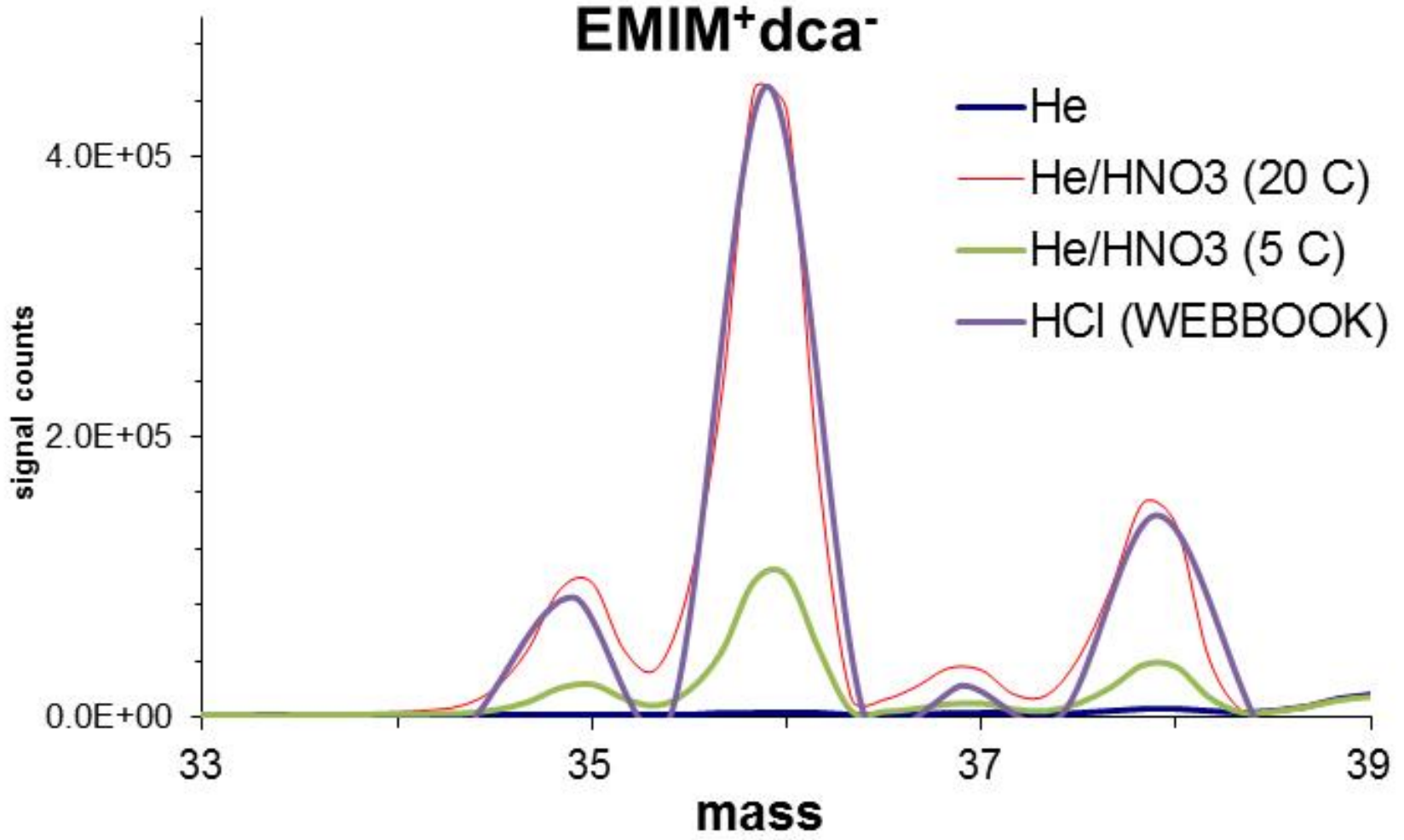
Comparison with reference HCl mass spectrum



Masses 35-38 are likely $^{35}Cl^+$, $H^{35}Cl^+$, $^{36}Cl^+$ and $H^{37}Cl^+$

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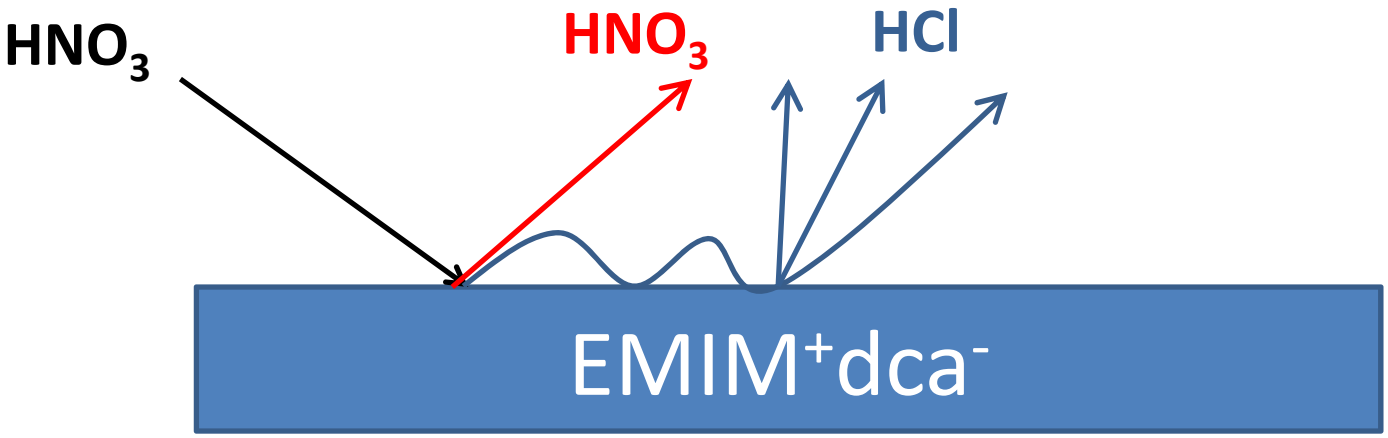
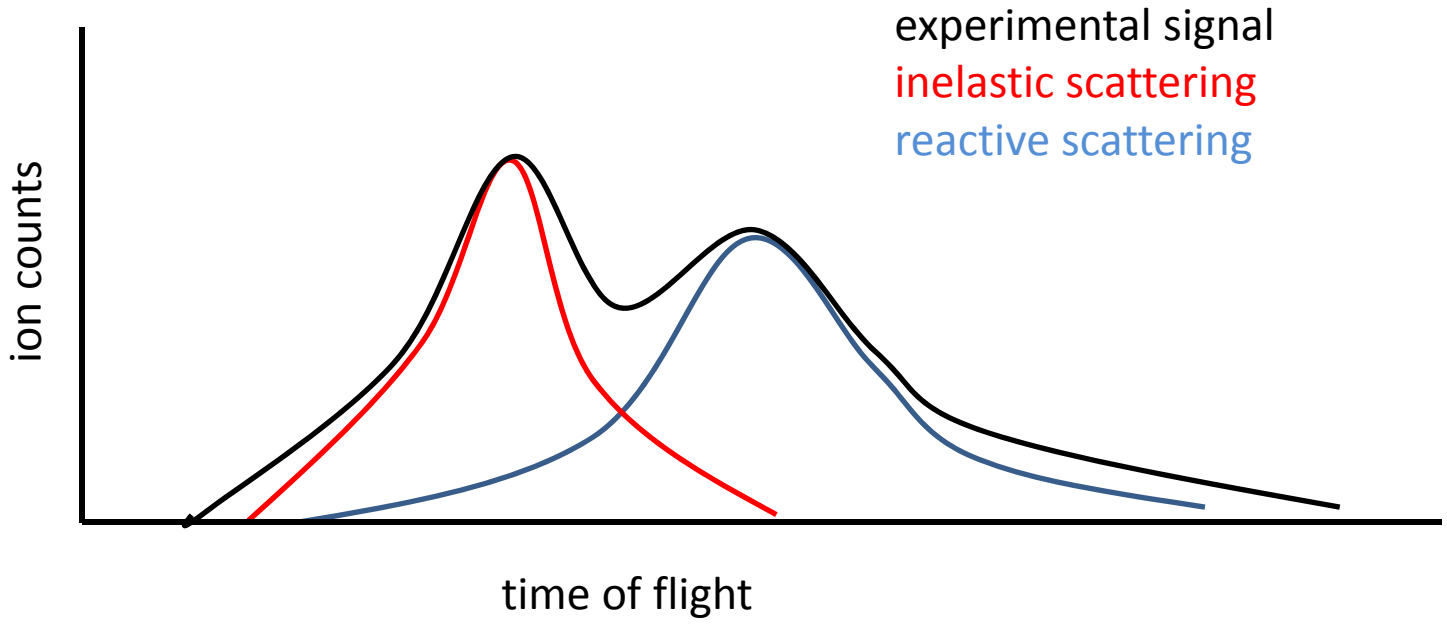
scattering processes





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Synthesis of dca^- ILs

- cation chloride salt prepared.
- Ag^+dca^- added and Ag^+Cl^- precipitates out.
  - 1000 ppm Cl^- remains as an impurity.
- Halide-free synthesis?

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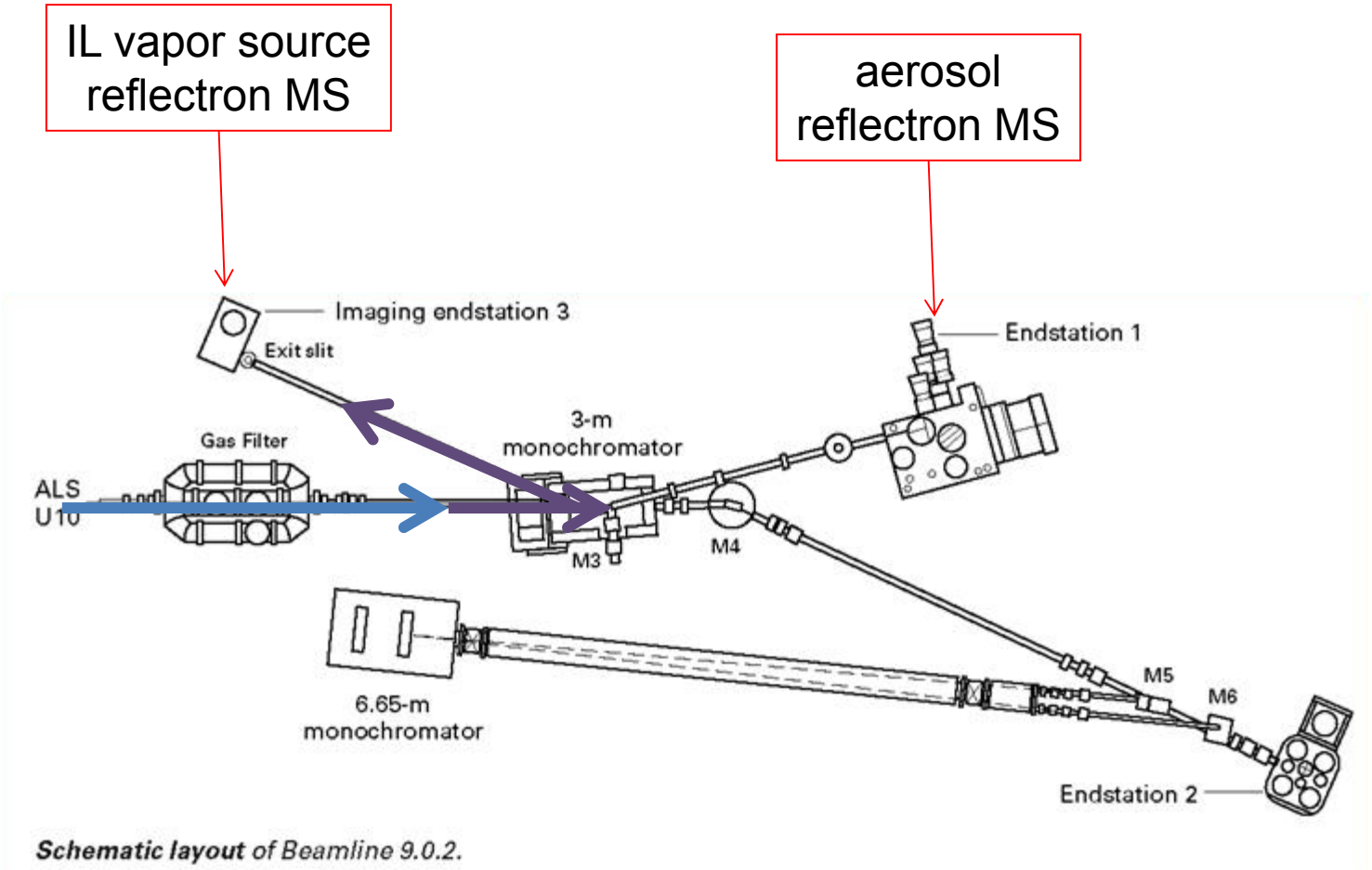
ALS: Chemical Dynamics Beamline



***Schematic layout** of Beamline 9.0.2.*

7.4-15.0 eV photons, 0.025 eV resolution

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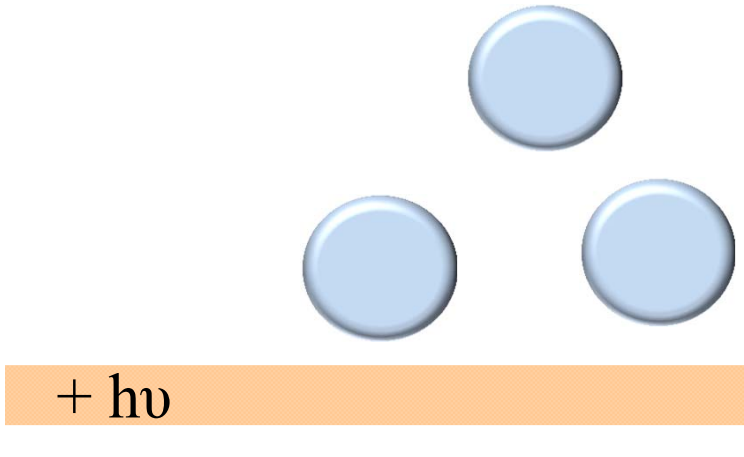
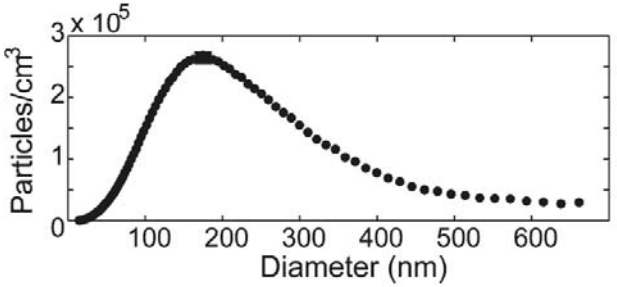
IL Aerosol reactivity

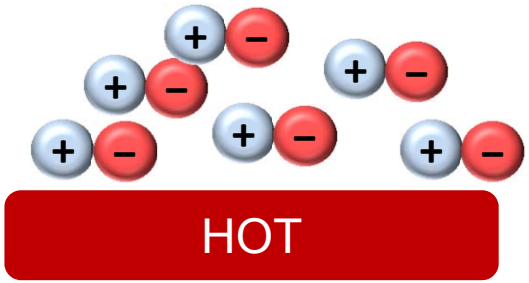
- ILs have very low vapor pressures:
  - Aerosols are liquid droplets suspended in gas phase:



- size distribution



Reaction dynamics and kinetics



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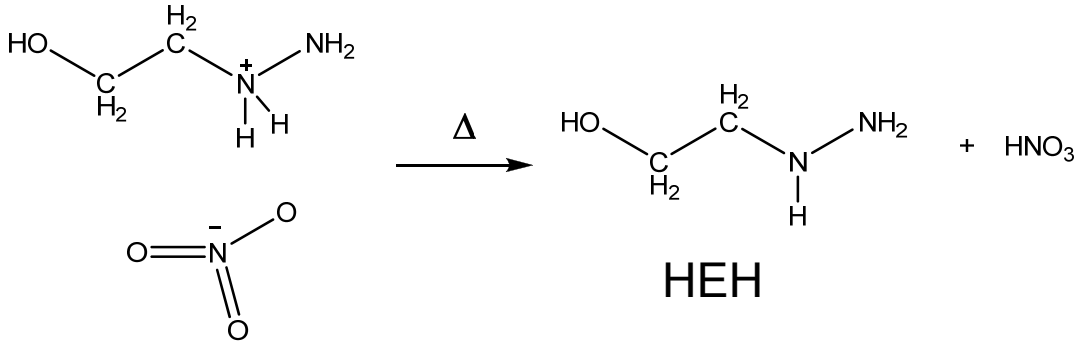
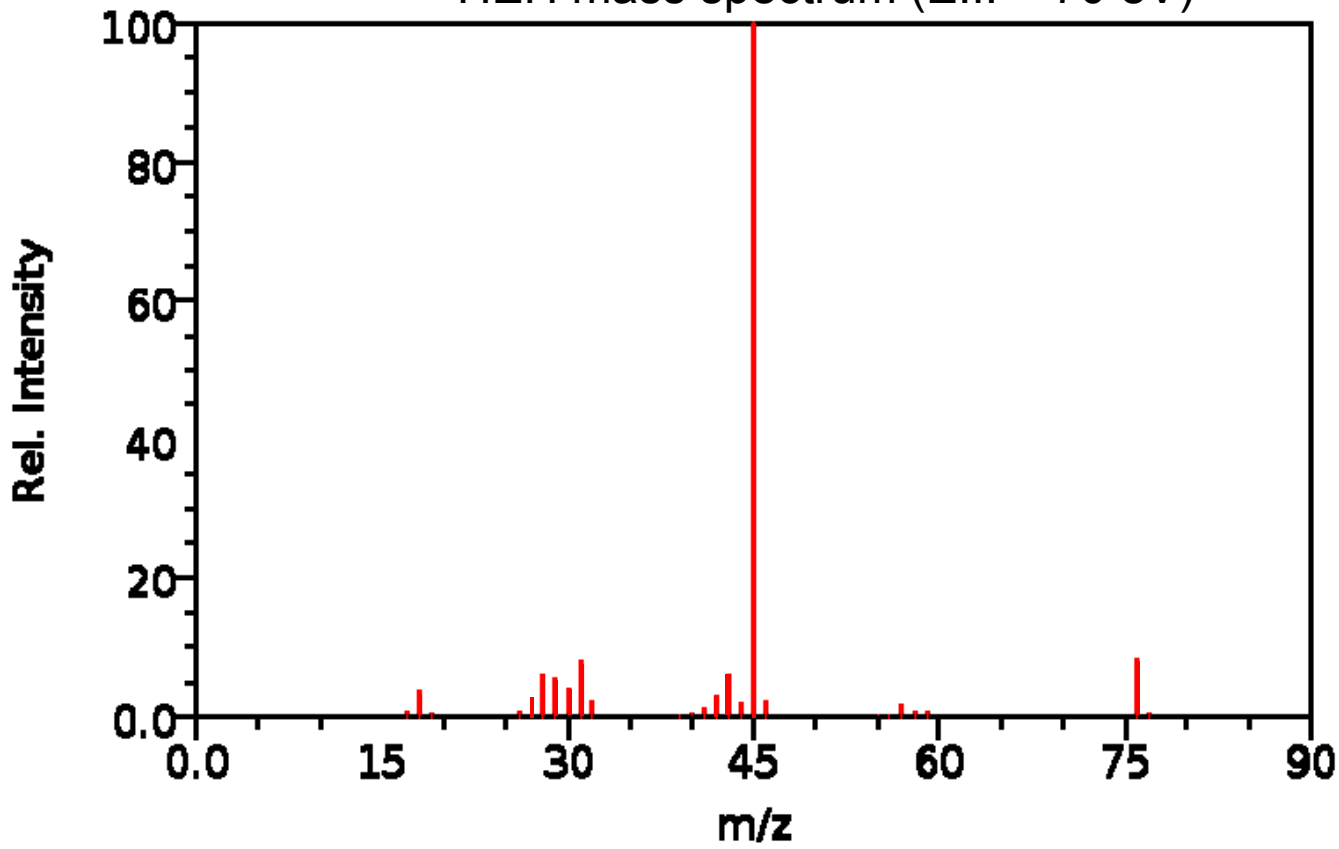


HEHN

HEH

HEH mass spectrum (E.I. ~ 70 eV)



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

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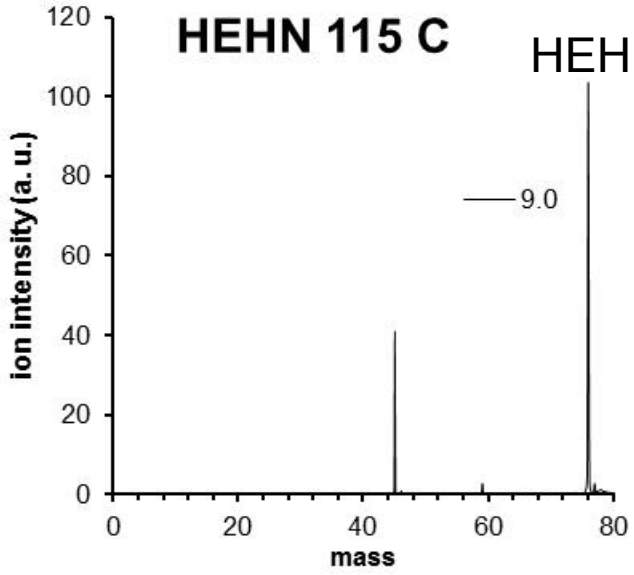

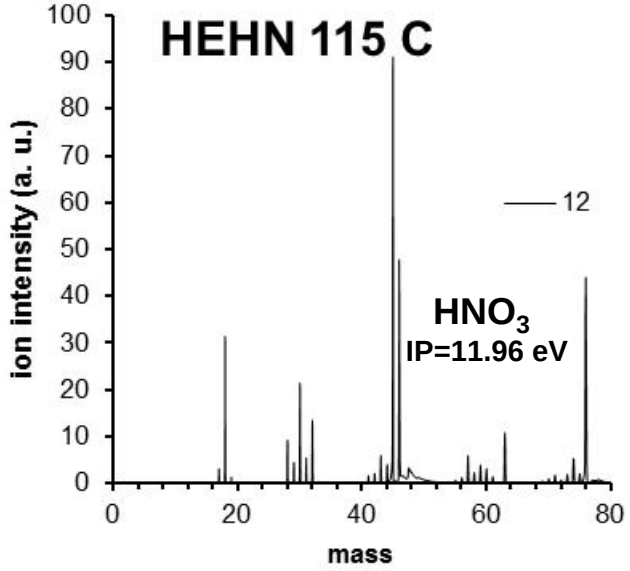

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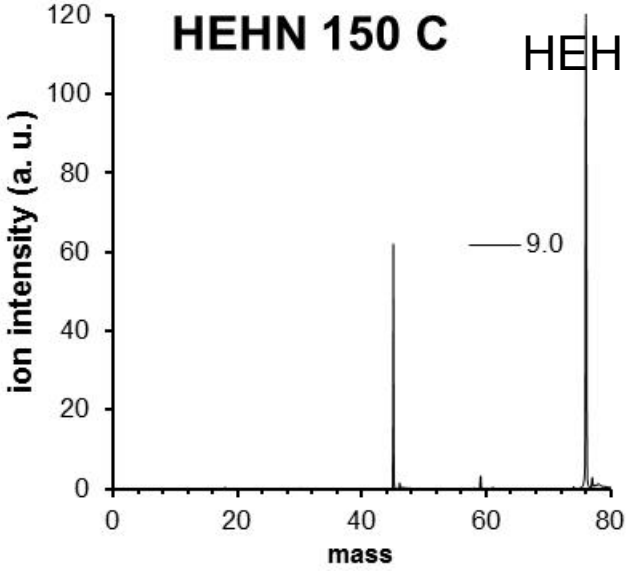

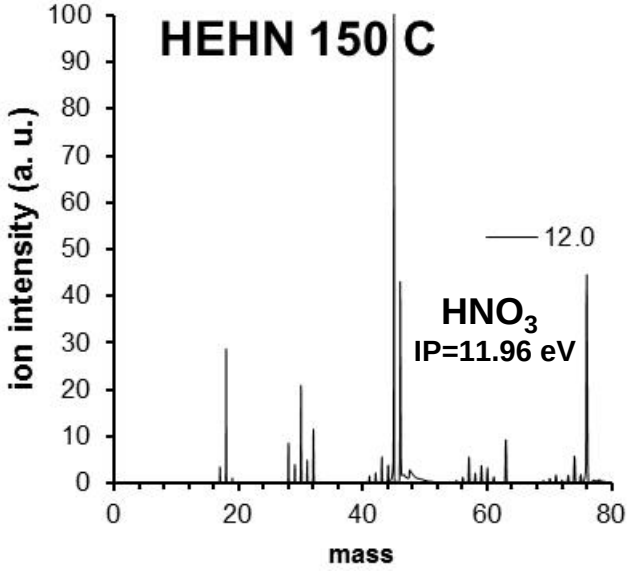

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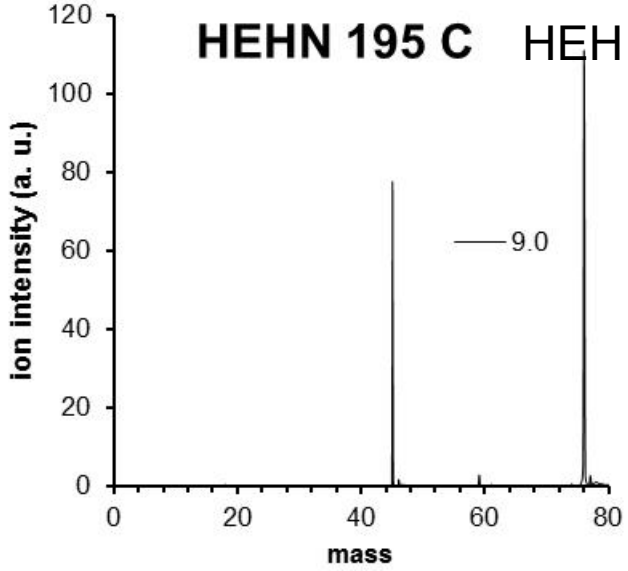

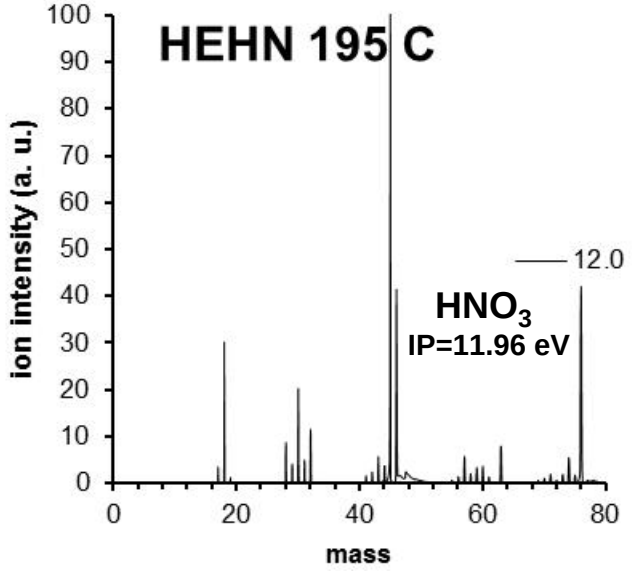

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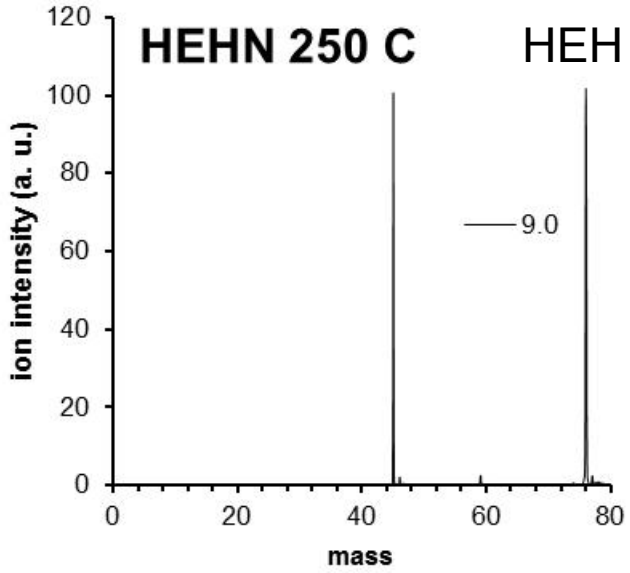

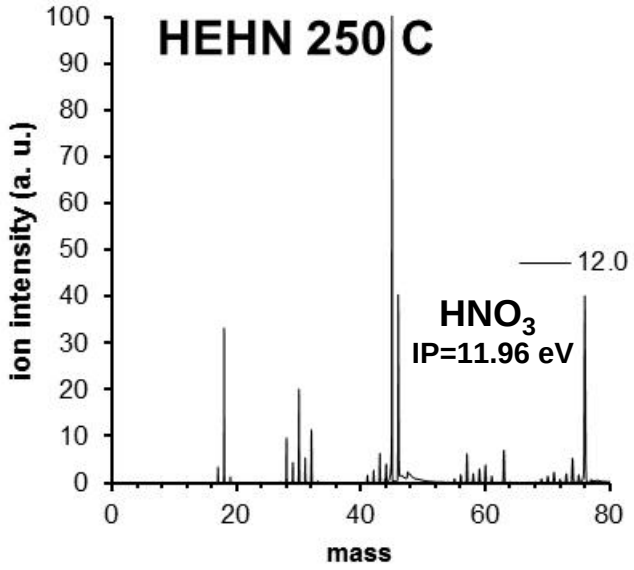

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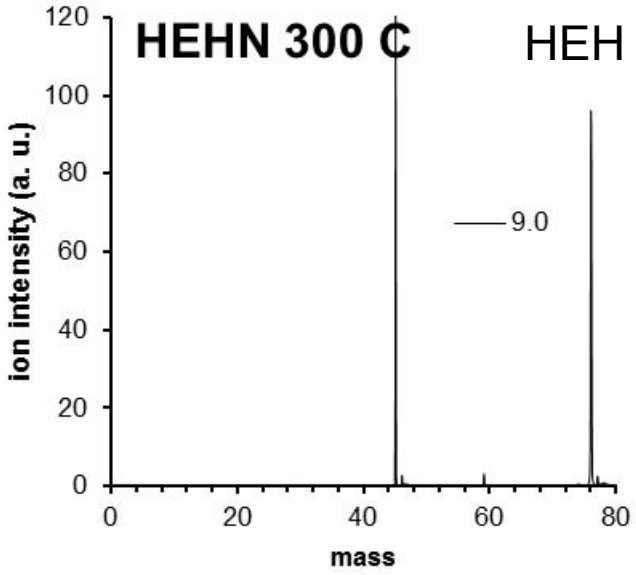

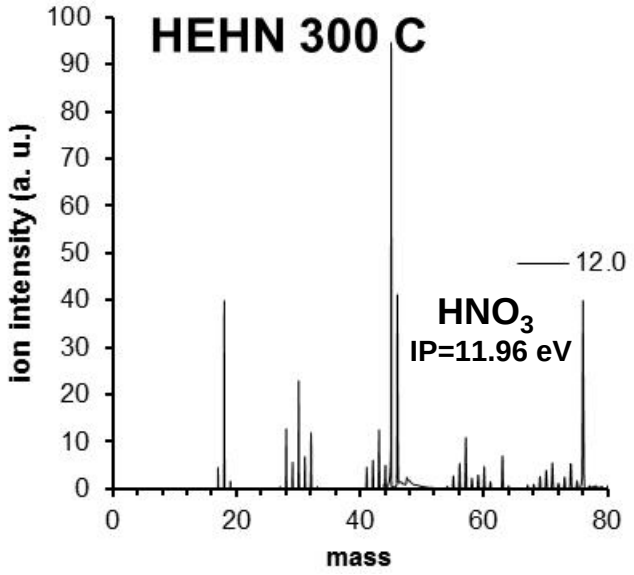

no HEH thermal decomposition products!

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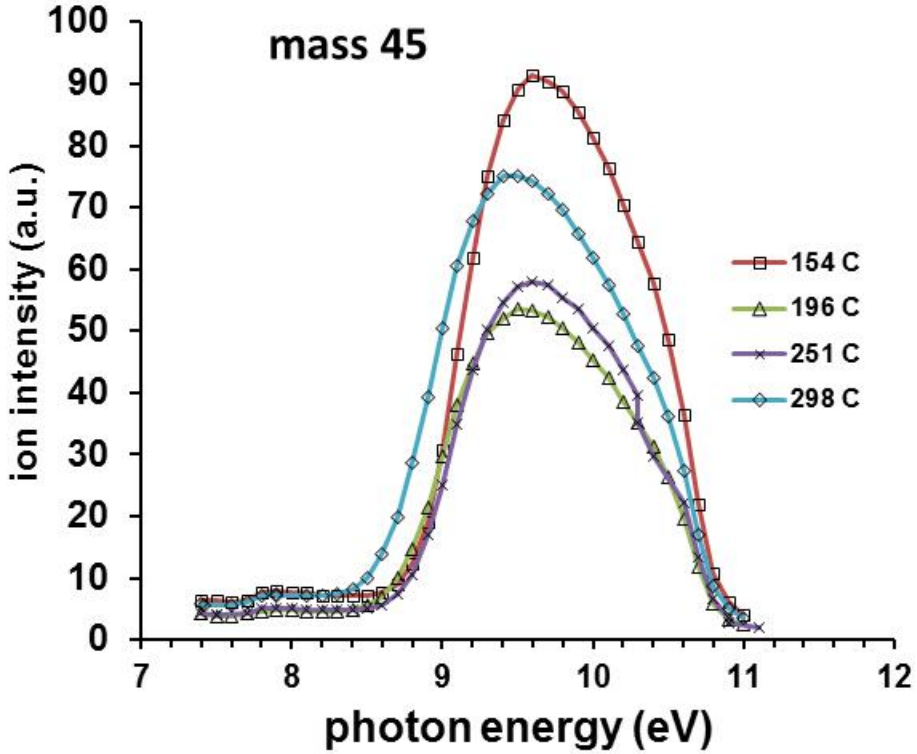

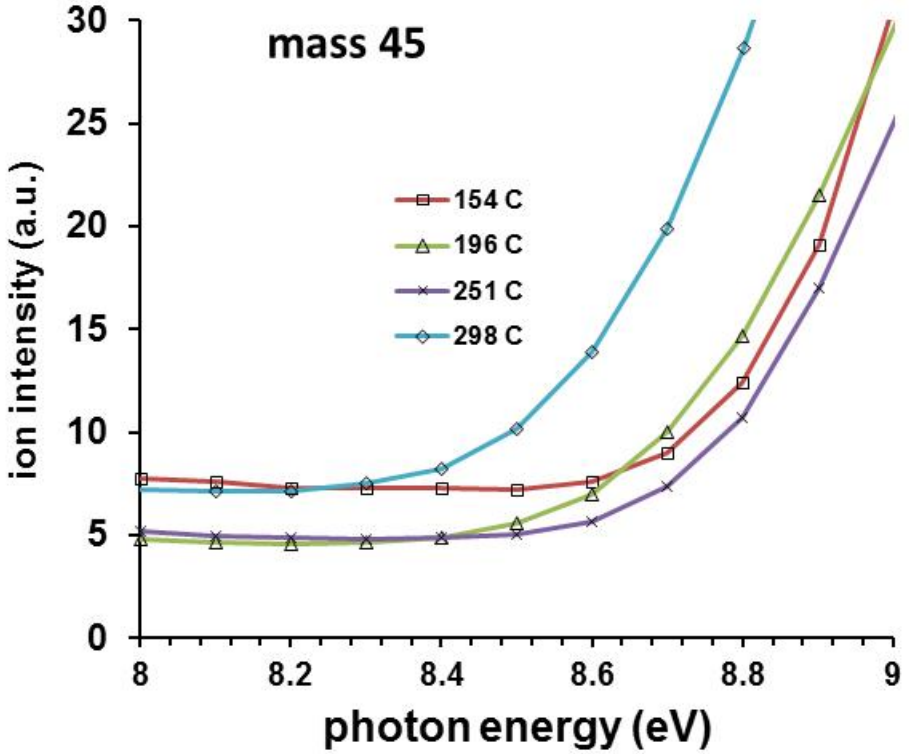

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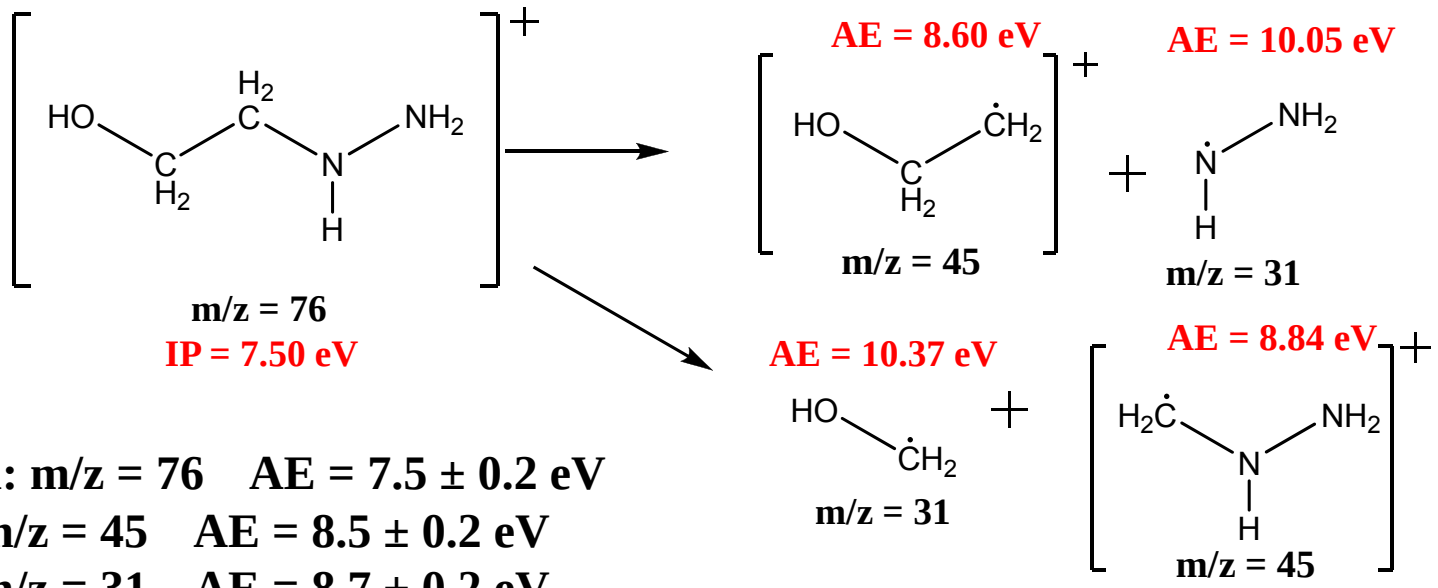
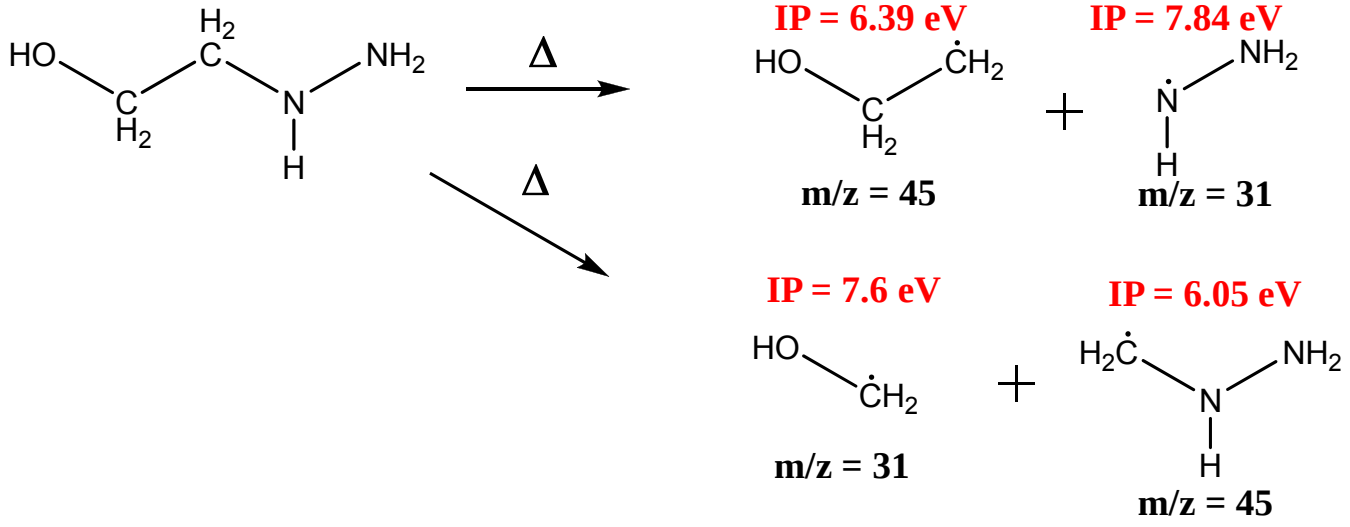
photoionization, fragmentation:



Experimental: m/z = 76 AE = 7.5 ± 0.2 eV
m/z = 45 AE = 8.5 ± 0.2 eV
m/z = 31 AE = 8.7 ± 0.2 eV

thermal decomposition, photoionization:



M06/6-31+G(d,p)

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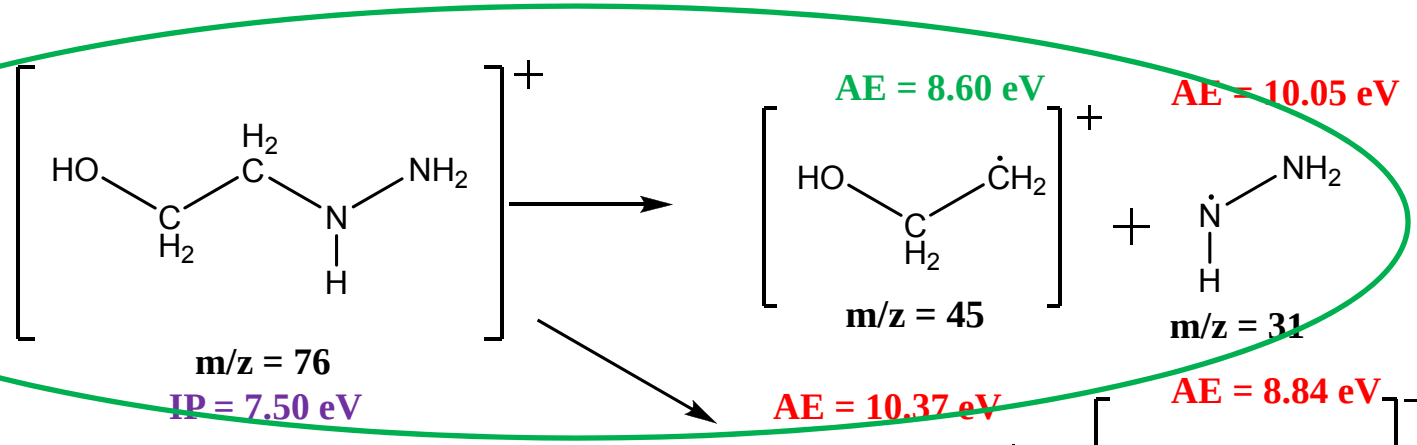
photoionization, fragmentation:



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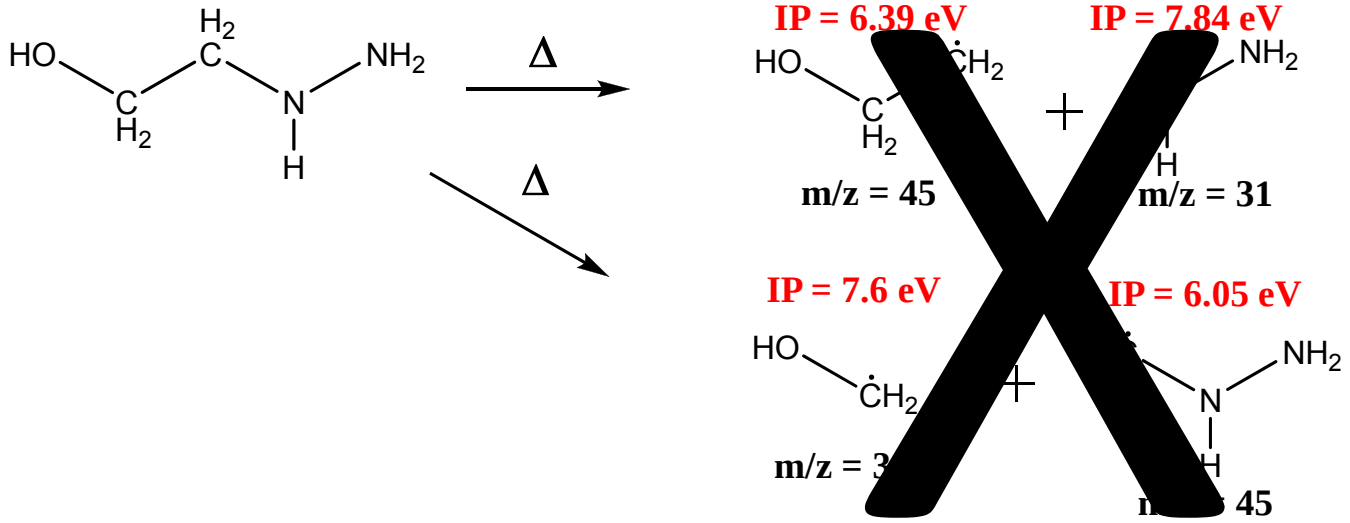
thermal decomposition, photoionization:



M06/6-31+G(d,p)

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Conclusions

- Basicity and nucleophilicity of anions in ILs can be predicted using GIL model.
- HNO_3 reacts very rapidly with Cl^- impurity in the ionic liquid to form HCl which vaporizes from the ionic liquid surface rapidly.
- Proton transfer in HEHN confirmed.

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Future plans

- Reactive scattering:
  - Obtain higher purity ionic liquid.
- VUV-PIMS:
  - HEHN on catalyst

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Acknowledgements

- Ionic Liquids Group:
  - Gammy Vaghjiani
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  - Amir Golan
  - Oleg Kostko
- Minton Group:
  - Vanessa Murray
  - Brody Bessire

AFOSR: Mike Berman

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Questions?!

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